Description

Fluororesin composition

~~Technical Field~~ Field of the Invention

The present invention relates to a fluororesin composition suitable for the molding of sliding ~~mechanic~~ mechanical parts etc. **[[**In**]]** The present invention more precisely **[[**it**]]** relates to a fluororesin composition which has lubricity, and further has superior friction and ~~wearing~~ wear resistance and compression creep resistance.

~~Technical background~~ Description of the Related Art

In the field of precision machines such as computer-related devices, office equipment or audio visual system related devices, etc., **[[**much**]]** many plastic products having sliding property are used for parts such as gears, bearings, sleeves, rolls, rails. In the past, such sliding parts were molded using a thermoplastic resin such as polyolefin, polyamide, fluororesin, ABS resin and polyphenylene sulfide; a thermosetting resin such as epoxy resin and phenolic resin; or a resin composition ~~combined~~ containing filler, such as glass fiber, carbon fiber and mica combined with such resins for raw materials, and various shapes of products have been produced.

However, as **[[**use**]]** conditions of using those parts has become severe, parts which have not only lubricity and heat resistance but also ~~is hard to be worn~~ resist wear due to friction and ~~is hard to be deformed~~ resist deformation even under strong stress have been demanded. By the way, there is a description that a resin composition containing zinc oxide whisker as filler can be used for molding materials ~~of electricity~~ for electrical parts because it is superior in static electricity diffusion property and sliding property, in Japanese Patent No.3041071. However, from a point of view to ~~wearing~~ wear resistance and compression creep resistance, more improvement **[[**to**]]** in the molded materials is demanded.

~~Disclosure of the present invention~~ Brief Summary of the Invention

[[The**]]** An object of the present invention is to provide a resin composition suitable for molding of sliding parts that **[[**have**]]** has lubricity and heat-resistant property and is further superior in friction and ~~wearing~~ wear resistance and compression creep resistance.

The present invention relates to a fluororesin composition comprising ~~tetrafluoroetylene~~ tetrafluoroethylene polymer, zinc oxide whisker and granular filler having average particle size of not more than 200μm and/or fibrous filler having average fiber length of not more than 500μm.

In the resin composition, the composition comprising 20-90% by weight of the tetrafluoroethylene polymer, 5-40% by weight of the zinc oxide whisker and 2-40% by weight of the filler, wherein the total quantity of the three components is 100% by weight, is a preferable embodiment.

Such a resin composition is superior in lubricity, heat-resistance, abrasion resistance to friction and compression creep resistance.

~~Preferable embodiments to implement the present invention~~
Detailed Description of the Invention

The present invention provides a fluororesin composition comprising tetrafluoroethylene polymer, zinc oxide whisker, and granular filler having average particle size of not more than 200μm and/or fibrous filler having average fiber length of not more than 500μm.

The tetrafluoroethylene polymer used in the present invention is homopolymer of tetrafluoroethylene (TFE) or tetrafluoroethylene copolymer obtained by copolymerizing TFE with copolymerizable monomers in **[[**the**]]** an amount of not more than 1.0% by weight. As the copolymerizable monomers, there can be used perfluoroalkene having 3 to 6 carbon atoms such as ~~hexafluoro propylene~~ hexafluoropropylene; perfluoro (alkyl vinyl ether) containing alkyl groups having 1 to 6 carbon atoms such as ~~perfluoro (propyl~~ perfluoro(propyl vinyl ether); or chlorotrifluoroethylene, etc.

Both homopolymer and the above-mentioned copolymer of TFE do not have melt-processability under ~~usual meltprocessing~~ typical melt-processing conditions because they have high melting **[[**point**]]** points.

The tetrafluoroethylene polymer can be used as molded articles for sliding parts, electric and electronic parts, packing materials, etc. as **[[**far**]]** long as it has the molecular weight that can be molded with compression molding and ~~others~~ other techniques. For example, when the property is shown by melting point instead of molecular weight, polymer having melting point of about 327 °C can be used suitably as molding resin for sliding parts which show good mechanical strength and heat resistance.

In addition, the tetrafluoroethylene polymers are used normally in a powder state for molding of various products. And the average particle size of the tetrafluoroethylene polymer is desirably in a range of not more than 100μm, preferably 5 to 100μm, more preferably 10 to 50μm.

The tetrafluoroethylene polymer having average particle size in the above range is superior in uniform mixing with the zinc oxide whisker and various types of fillers. Such a tetrafluoroethylene polymer can be produced as powder directly by suspension polymerization or emulsion polymerization, and may be produced by pulverizing pellet, that has been once pelletized after polymerization, to form powder having average particle size of not more than 100μm. In addition, powder of commercial molding grade can be used when it has the above average particle size.

In the zinc oxide whisker of the present invention, there is no particular limitation in the production method and shape. ~~Giving~~ As one ~~of examples~~ example, it can be produced by heat-treating **[[**the**]]** metal zinc powder having an oxidated membrane on its surface under an atmosphere containing oxygen. **[[**Thus**]]** The obtained whisker presents the shape of a so-called tetrapod-shaped, **[[**that**]]** needle-shaped crystal **[[**was**]]** expanded from a center of tetrahedron toward four directions. Length of the needle-shaped part is preferably 3-200μm and a base part diameter of needle-shaped part is preferably 0.1-10μm.

Zinc oxide whisker containing such a tetrapod-shaped whisker is preferable because it does not affect **[[**to**]]** properties such as lubricity, ~~wearing~~ wear resistance or compression creep resistance even when a needle-shaped part is partially damaged during mixing with each component constituting the resin composition or during molding the resin composition.

Further, the surface of the zinc oxide whisker can be treated with a silane-based, a chrome-based or a titanium-based coupling agent. When the surface of the zinc oxide whisker is treated with the silane-based coupling agent in particular, dispersibility of the whisker into tetrafluoroethylene polymer particle can be improved. Such a tetrapod-shaped zinc oxide whisker is commercially available in the market, for example, with trade name of Pana-Tetra from Matsushita Electric Industrial Co., Ltd., and can be obtained and used easily.

The above mentioned zinc oxide whisker contributes to formation of a composition having low anisotropy that is strengthened three dimensionally by the peculiar shape, and the molded articles showing good dimensional stability can be produced from the composition.

In addition, since the zinc oxide whisker itself shows good electroconductivity and ~~thermalconductivity~~ thermal conductivity, it can effectively radiate frictional heat generated when the molded articles **[[**is slid**]]** slides. It seems that the feature of the zinc oxide whisker is combined with various characteristics of other fillers used together to generate synergistic effects and consequently enhance friction and ~~wearing~~ wear resistance and compression creep resistance.

Furthermore, the Mohs hardness degree of the zinc oxide whisker is about 4 and this shows zinc oxide as a comparatively soft material, so it is possible to reduce wear of a partner soft material and also to reduce self wear, and further to prevent a performance decline due to the damage caused by extrusion deformation of the articles.

In the present invention, the filler combined with the tetrafluoroethylene polymer in conjunction with zinc oxide whisker is inorganic substances or organic substances, and has the average particle size of not more than

200μm, preferably 2 to 50μm and/or average fiber length of not more than 500μm.

As preferable examples of the fillers of the present invention, at least one substance selected from the group of carbon fiber, coke powder, graphite powder, bronze powder, copper powder, zinc oxide powder, talc, glass fiber, molybdenum disulfide, a polyamide, an aromatic polyamide, and polyphenylene sulfide. Above all, a carbon fiber, coke powder, graphite powder, bronze powder, copper powder, zinc oxide powder, talc, glass fiber are preferable. In the present invention, if fillers have the above average particle size and/or the average fiber length, commercially available products can be used as they are.

As for ratios of each component constituting resin compositions, it is desirable that the tetrafluoroethylene polymer is preferably in the range of 20-90% by weight, more preferably 25-80% by weight, the zinc oxide whisker is preferably in the range of 5-40% by weight, more preferably 10-30% by weight and the filler is preferably in a range of 2-40% by weight, more preferably 10-35% by weight. Total quantity of above three components ~~becomes~~ is 100% by weight **[[**here**]]**. When each component is in the above range, the resin composition showing excellent superior friction and ~~wearing~~ wear resistance and compression creep resistance while retaining good lubricity can be obtained, and the compositions are suitable for molding of sliding parts.

Stabilizers and additives such as anti-oxidants, thermal stabilizers, weather stabilizers, flame retardants, and pigments can be combined with the resin compositions to the extent that they do not impair the object of the present invention.

By mixing powder uniformly, to which the above stabilizers or additives are added as required, with three components of the present invention using conventionally known mixing device such as a ~~Henshel~~ Henschel mixer, a powdery resin composition can be obtained.

From such a powdery resin composition, various sliding parts as required can be produced by a compression molding method or an extrusion molding method.

For example, the above resin composition is preformed by a compression molding method and sintered at the temperature over melting point of the tetrafluoroethylene polymer to form molded materials. Then the materials are shaped by curving etc. in accordance with the required article to form the final parts.

Since the resin compositions of the present invention are composed with the zinc oxide whisker and at least one kind of fillers **[[**are**]]** is dispersed uniformly in the tetrafluoroethylene polymer, the resin composition maintains good lubricity and further shows excellent friction and ~~wearing~~ wear resistance and compression ~~creeping~~ creep resistance.

In addition, the resin compositions have stable static electricity diffusibility and are suitable as raw resin materials for various kinds of sliding parts, electric and electronic parts, packing materials, etc.

Examples

The present invention will be explained by using examples in more detail but it is not limited to the examples.

At first, raw materials used are shown below.

(a) Tetrafluoroethylene homopolymer: It is abbreviated PTFE.
Average particle size 35μm, Melting point 327°C
Product from DuPont · **[[**Mitui**]]** Mitsui Fluorochemicals Co, Ltd.
Grade name: Teflon (registered trade mark) 7-J

(b) Zinc oxide whisker:
Diameter of a needle-shaped staple fiber 0.2 to 30μm
Length of a needle-shaped staple fiber 2 to 50μm.
Product from Matsushita Electric Industrial Co., Ltd.
Trade name: Pana-Tetra

(c) Carbon fiber:
Average fiber diameter 14.5μm, Average fiber length 120μm
Product from Kureha Chemical Industry Co. Ltd.

(d) Copper powder:

Average particle size 26μm

Product from Fukuda Metal Foil & Powder Co. Ltd.

(e) Graphite powder:

Average particle size 20μm

Product from Oriental Sangyo Co. Ltd.

(f) **[[**Cokes**]]** Coke powder:

Average particle size 20μm

Product from Nippon Carbon Co. LTD

(g) Glass fiber:

Average fiber diameter 10.5μm, Average fiber length 20μm

Nitto Boseki Co. Ltd.

(Examples 1 to 5) (Comparative Examples 1 to 5)

The tetrafluoroethylene homopolymer, zinc oxide whisker and various fillers are used **[[**at**]]** as summarized in table 1 and they are mixed uniformly using a ~~Henshell~~ Henschel mixer to obtain the resin compositions.

Each resin composition obtained was preformed under pressure of 70 MPa or 700**[[**MPa**]]** kg/cm^2 and then sintered at 370°C for three hours to obtain a cylinder-shaped molded article of a diameter of 50mm height of 100mm.

~~Wearing~~ Wear loss, compression ~~creeping~~ creep property and sliding temperature of each molded article were measured by test methods mentioned below and the results are shown in Table 1.

(1) ~~Wearing~~ Wear loss:

A ring having outer diameter of 25.7mm, inner diameter of 20mm and height of 20mm is prepared from the cylinder-shaped molded article mentioned above and used as a specimen for the test.

~~Wearing~~ Wear loss of the specimen was measured using twin type friction and ~~wearing~~ wear tester (product from INTESCO Co. Ltd.) in accordance with JIS K7218 (A method). Measurement of ~~wearing~~ wear loss was conducted by sliding for 24 hours under each ~~wearing~~ wear test conditions of the partner material, the load and the sliding speed described in table 1. The ~~wearing~~ wear loss after the test is calculated from coefficient of ~~wearing~~ wear and coefficient of ~~frictional~~ friction.

(2) Compression ~~creeping~~ creep property:

A cube having side length of 12.7mm was prepared by curving 1.0 the above cylinder-shaped molded article and was used as a test specimen.

Compression ~~creeping~~ creep property was measured using ~~six-liked~~ six-linked compression ~~creeping~~ creep tester (product from ORIENTEC Co., Ltd.) in accordance with ASTM D-621 under conditions of measurement temperature at 23°C and load of 140kgf/cm^2. In table 1, MD shows a compression direction, and CD shows a vertical direction which is a right angle to the compression direction.

Values of deformation show the rests of value that quantity of recovery after 24 hours was deducted from all volume of deformation.

(3) Sliding temperature:

A tip of thermocouple was set on about 2mm upper parts from the sliding side of the partner material using EFM-3F type machine produced by ORIENTEC Co. Ltd. and measurement was conducted.

Table 1

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Comp. Ex.1	Comp. Ex.2	Comp. Ex.3	Comp. Ex.4	Comp. Ex.5	Comp. Ex.6	Comp. Ex.7
Resin composition (wt %)												
•PTFE	80.0	70.0	55.0	57.0	70.0	100	90.0	80.0	90.0	70.0	67.0	80.0
•Zinc oxide whisker	10.0	15.0	20.0	10.0	10.0	-	10.0	20.0	-		-	
•Carbon fiber	10.0	15.0	10.0	•		-	-	-	10.0	15.0	-	-
•Copper powder	-		15.0	-	-	-	-	-	-	15,0	-	-
•Coke powder	-	-	-	31.0	-	-	-	-	-		31.0	-
•Graphite	-	-	-	2.0	-	-	-	-	-	-	2.0	-
•Grass fiber	-	-	-	-	20.0	-	-	-	-	-	-	20.0
~~Wearing~~ Wear test result												
•Test condition												
-Partner material (*)	ADC-12	ADC-l2	ADC-12	FC-25	SS-41	ADC-12	ADC-12	ADC-12	ADC-l2	ADC-12	FC-25	SS-41
• Load (kg/cm.2)	8.0	8.0	8.0	6.0	6.0	8.0	8.0	8.0	8.0	8.0	6.0	6.0
•Sliding speed (m/s)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
• ~~Wearing~~ Wear coefficient(**)(x 10-)	14.2	11.5	4.8	9.0	7.2	2791	14.1.	5.9	46.0	12.1	49.3	12.6
•Friction coefficient (**)	0.226	0.193	0.255	0.288	0.36	0.1.85	0.203	0.285	0.252	0.244	0.348	0.:37
A sliding temperature(°C)	76	75	83	78	93	73	80-82	88-90	95	85	133	143
Compression ~~creeping~~ creep test result(%)												
•24hours deform (MD)	6.4	4.9	3.5	3.5	11.2	14.0	11..0	7.7	9.4	5.8	4.9	1.2.4
-24hours deform (CD)	7.6	5.3	3.2	3.1	13.3	15.8	12.1,	9.5	1.3.2	6.0	3.9	1:3.7
-~~Eternity~~ Permanent deformation (MD)	3.2	2.6	1.7	1.7	6.5	7.6	6.4	4.3	5.1	:3.1	1.8	7.1
•~~Eternity~~ Permanent deformation (CD)	3.9	2.9	1.7	1,4	7.8	8.6	6.9	5.7	7.1	:3.0	1.8	8.2

*Partner material: ADC-12 [An aluminum alloy die-casting JIS H5302(1976)]
FC [4 kinds of Gray cast iron JIS G5501(1976)]
SS-41 [Rolled steel materials for general structure JIS G3101(1976)]

** Unit of Friction coefficient and ~~wearing~~ wear coefficient:$cm^3 \cdot sec/kg \cdot m \cdot hr$

As is clear from the results of table 1, it is found that since the resin composition of each of the Examples comprising the tetrafluoroethylene polymer, the zinc oxide whisker and the fillers has extremely good thermal conductivity by contribution of a zinc oxide whisker ~~comparing~~ compared with resin compositions of each of the comparative examples that consisted of a tetrafluoroethylene polymer alone or with various fillers, the sliding temperature can be lowered, the coefficient of friction ~~keeps~~ can be kept constantly low and the ~~wearing~~ wear coefficient becomes smaller, and the compression ~~creeping~~ creep property shows a small value.

Applicability to industries

By the present invention, the resin compositions suitable for molding of sliding parts and others that have lubricity and thermal-resistant property and are further superior in friction and ~~wearing~~ wear resistance and compression creep resistance.

The resin compositions obtained by the present invention are superior in lubricity, thermal-resistance, friction and ~~wearing~~ wear resistances and compression creep resistance.

Since the resin compositions of the present invention have the construction that the zinc oxide whisker and at least one kind of fillers are dispersed uniformly in the tetrafluoroethylene polymer, the resin compositions maintain good lubricity and further ~~shows~~ show excellent friction and ~~wearing~~ wear resistances and compression ~~creeping~~ creep resistance. Therefore the resin compositions have stable static electricity diffusibility and are suitable as resin materials resin for various kinds of sliding parts, electric and electronic parts, packing materials, etc.